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(54) **Invisible inkjet ink printing system**

(57) An invisible inkjet ink printing system (20) includes an invisible inkjet ink composition that prints an "invisible" image (85) which is substantially invisible in ordinary ambient light (88) yet viewable (86) under ultraviolet lighting conditions, such as with a "black light" (90). The invisible inkjet ink composition comprises an aqueous ink vehicle and about 0.1 to 4 wt% of at least one invisible fluorescing dye. The invisible fluorescing dyes tested include: sodium flourescein; 2,7-dichlorofluorescein; resorufin; rhodamine 6G; eosin Y, sodium salt; 7-hydroxycoumarin; harmine; and phloxine B. Methods of making and using such an invisible inkjet ink composition are also provided, along with an invisible ink inkjet printing mechanism (20). Images visible under ambient light (82,84) may also be printed with the same inkjet printing mechanism (20) in conjunction with printing the invisible image (85).

FIG. 1

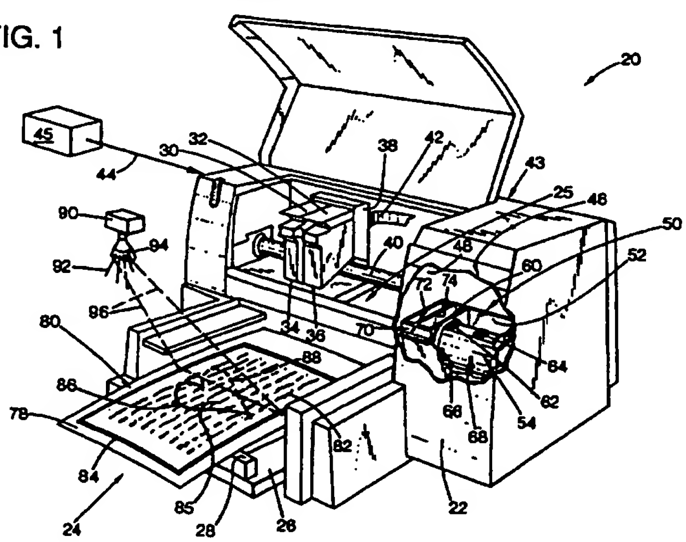

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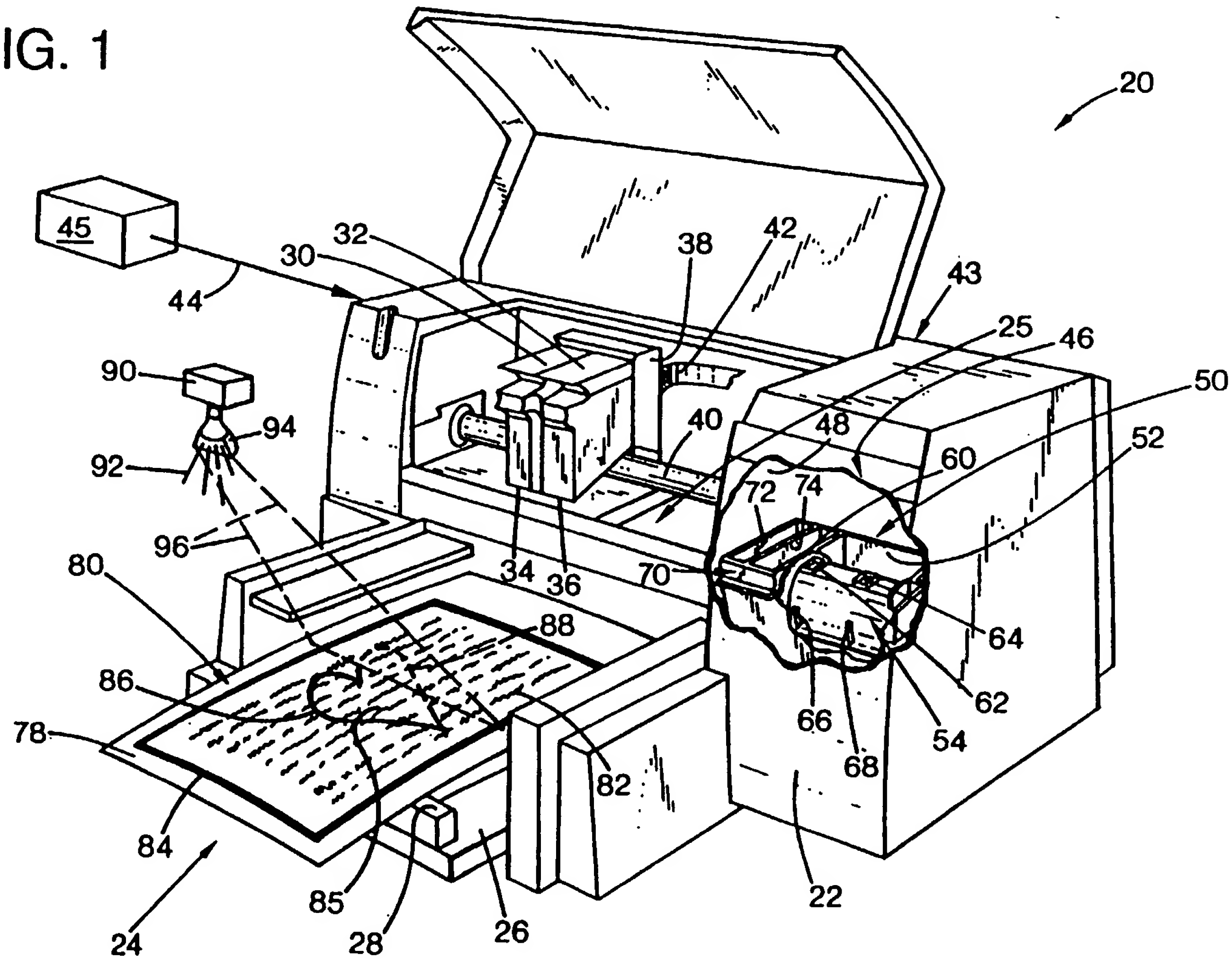
FIG. 1



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INVISIBLE INKJET INK PRINTING SYSTEM

Field of the Invention

This invention relates generally to inkjet ink compositions used for printing by an inkjet printing mechanism, and more particularly to an invisible inkjet ink composition, substantially invisible in ordinary light yet viewable under special ultraviolet ("uV") lighting conditions, such as with a "black light," and to methods of making and using such an invisible inkjet ink composition.

Background of the Invention

Inkjet printing mechanisms use cartridges, often called "pens," which shoot drops of liquid colorant, referred to generally herein as "ink," onto a page. Each pen has a printhead formed with very small nozzles through which the ink drops are fired. To print an image, the printhead is propelled back and forth across the page, shooting drops of ink in a desired pattern as it moves. The particular ink ejection mechanism within the printhead may take on a variety of different forms known to those skilled in the art, such as those using piezo-electric or thermal printhead technology. For instance, two earlier thermal ink ejection mechanisms are shown in U.S. Patent Nos. 5,278,584 and 4,683,481, both assigned to the present assignee, Hewlett-Packard Company. In a thermal system, a barrier layer containing ink channels and vaporization chambers is located between a nozzle orifice plate and a substrate layer. This substrate layer typically contains linear arrays of heater elements, such as resistors, which are energized to heat ink within the vaporization chambers. Upon heating, an ink droplet is ejected from a nozzle associated with the energized resistor. By selectively energizing the resistors as the printhead moves across the page, the ink is expelled in a pattern on the print media to form a desired image (e.g., picture, chart or text).

To clean and protect the printhead, typically a "service station" mechanism is mounted within the printer chassis so the printhead can be moved over the station for maintenance. For storage, or during non-printing periods, the service stations usually

include a capping system which hermetically seals the printhead nozzles from contaminants and drying. Some caps are also designed to facilitate priming, such as by being connected to a pumping unit that draws a vacuum on the printhead. During operation, clogs in the printhead are periodically cleared by firing a number of drops of ink through each of the nozzles in a process known as "spitting," with the waste ink being collected in a "spittoon" reservoir portion of the service station. After spitting, uncapping, or occasionally during printing, most service stations have an elastomeric wiper that wipes the printhead surface to remove ink residue, as well as any paper dust or other debris that has collected on the printhead.

In aqueous-based ink compositions, ink is typically formulated by dissolving dye in an ink vehicle. For example, a yellow ink would comprise a yellow dye dissolved in an ink vehicle. The dye molecules employed in inkjet ink compositions are often in the form of dye salts made of a dye anion and a cation such as sodium. These dyes are designed to form solids in the target paper substrate by way of crystallization of the dye salt. In color inkjet printers, typically three colors are used, cyan, yellow and magenta, which in certain combinations form all the colors of the rainbow. Applying all three colors of ink at a single location produces what is known as a "process" black. Many inkjet printers have an additional cartridge containing a "true" black ink.

In addition to the standard colors of cyan, yellow, magenta and black inks, it would be desirable in some specialty applications to have an "invisible" ink, which as used herein, refers to an ink that cannot be detected under normal lighting conditions, but instead under ultraviolet lighting. Such invisible inks may be useful for a variety of purposes, such as invisible bar codes, invisible security markings, or other covert marking and recording needs. Until now, such invisible inks have not been commercially available to consumers in inkjet printing mechanisms or other commercial printing devices.

Summary of the Invention

According to one aspect of the invention, an invisible inkjet ink composition is provided for printing in an inkjet printing mechanism. The invisible inkjet ink composition consists essentially of an aqueous ink vehicle and about 0.1 to 4 wt% of at least one invisible fluorescing dye, which when mixed and printed through the inkjet printing mechanism produce an image that is substantially invisible in ordinary ambient lighting conditions and viewable under ultraviolet lighting conditions. In a more preferred embodiment, about 0.01 to 0.10 wt% of at least one invisible fluorescing dye is mixed with an aqueous ink vehicle known to be compatible with commercially available dye-based color inkjet inks and a pigment-based black inkjet ink.

According to another aspect of the invention, a set of thermal inkjet inks is provided for printing an image with an inkjet printing mechanism, with the printed image being substantially invisible in ordinary ambient lighting conditions and viewable under ultraviolet lighting conditions. The set of thermal inkjet inks includes a first ink, a second ink, and a third ink. Each of the first, second and third inks has about 0.01 to 4 wt% of at least one dye selected from the group comprising: (1) sodium flourescein; (2) 2,7-dichlorofluorescein; (3) resorufin; (4) rhodamine 6G; (5) eosin Y, sodium salt; (6) 7-hydroxycoumarin; (7) harmine; and (8) phloxine B. Each of the first, second and third inks also has the following components: about 3 to 20 wt% of at least one diol; 0 to about 5 wt% of at least one glycol ether; about 3 to 9 wt% of 2-pyrrolidone; about 0.5 to 5 wt% of at least one component selected from the group consisting of surfactants, buffers, and biocides; about 3 to 11 wt% of at least one inorganic salt; and the balance water.

According to a further aspect of the invention, a method for invisible printing is provided using an inkjet printing mechanism to produce a hardcopy output having an invisible image that is substantially invisible in ordinary ambient lighting conditions and viewable under ultraviolet lighting conditions. This method includes the steps of positioning a print media in a printzone of the printing mechanism, and printing on the print media in the printzone with an invisible inkjet ink composition consisting essentially of an aqueous ink vehicle and about 0.01 to 4 wt% of at least one invisible

fluorescing dye. In the illustrated embodiment, the at least one invisible fluorescing dye may be selected as sodium flourescein, 2,7-dichlorofluorescein, resorufin, rhodamine 6G, eosin Y (sodium salt), 7-hydroxycoumarin, harmine, and phloxine B.

According to yet another aspect of the invention, an invisible ink inkjet printing mechanism includes a chassis, and a printhead mounted to the chassis to print in a print zone. The printhead has plural nozzles selectively fired to print a selected invisible image on a print media page in the printzone in response to a control signal. The invisible ink inkjet printing mechanism also has an invisible inkjet ink composition dispensed by the printhead. The invisible inkjet ink composition consists essentially of an aqueous ink vehicle and about 0.01 to 4 wt% of at least one invisible fluorescing dye to produce the selected invisible image which is substantially invisible in ordinary ambient lighting conditions and viewable under ultraviolet lighting conditions.

An overall goal of the present invention is to provide an invisible inkjet ink composition for use in printing mechanism, that is, an ink which is substantially invisible in ordinary light yet viewable under special ultraviolet lighting conditions.

Another goal of the present invention is to provide a dye set made up of at least three different colors of such an invisible inkjet ink composition.

A further goal of the present invention is to provide a method of making such an invisible inkjet ink composition.

An additional goal of the present invention is to provide an invisible inkjet printing mechanism using such an invisible inkjet ink composition.

Brief Description of the Drawing

FIG. 1 is a partially schematic, perspective view of one form of an invisible ink dispensing inkjet printing mechanism, here shown as an inkjet printer, using one form of an invisible inkjet ink composition of the present invention to generate a hardcopy output, illustrated in conjunction with an ultraviolet light source illuminating a portion of the hardcopy output.

Detailed Description of the Preferred Embodiments

FIG. 1 illustrates an embodiment of an invisible inkjet ink printing system having an inkjet printing mechanism, here shown as an invisible ink inkjet printer 20 constructed in accordance with the present invention. The printer 20 may be used for printing for business reports, correspondence, desktop publishing, and the like, in an industrial, office, home or other environment, as well as for printing invisible images which are substantially invisible in ordinary light yet viewable under special ultraviolet ("uV") lighting conditions. A variety of inkjet printing mechanisms are commercially available. For instance, some of the printing mechanisms that may embody the present invention include plotters, portable printing units, copiers, cameras, video printers, and facsimile machines, to name a few. For convenience the concepts of the present invention are illustrated in the environment of an inkjet printer 20.

While it is apparent that the printer components may vary from model to model, the typical inkjet printer 20 includes a chassis 22 and a print medium handling system 24 for supplying sheets of print media to the printer 20. The print media may be any type of suitable sheet material, such as paper, card-stock, transparencies, fabric, mylar, foils, and the like, but for convenience, the illustrated embodiment is described using paper as the print medium. The print medium handling system 24 moves the print media into a print zone 25 from a feed tray 26 to an output tray 28, for instance using a series of conventional motor-driven rollers (not shown).

In the print zone 25, the media sheets receive ink from an inkjet cartridge, such as a single-color or monochrome ink cartridge 30 and a tri-color ink cartridge 32. The cartridges 30, 32 are also referred to as "pens" by those in the art. In some embodiments, the illustrated tri-color pen 32 may be replaced by a group of discrete monochrome pens may be used, along with a fourth monochrome pen containing black ink. The pens 30, 32 are transported by a carriage 38 which may be driven along a guide rod 40 by a conventional drive belt/pulley and motor arrangement (not shown). The pens 30, 32 selectively deposit one or more ink droplets on the print media page in accordance with instructions received via a conductor strip 42 from a printer controller, such as a microprocessor which may be located within chassis 22 at the area indicated generally by arrow 43.

The controller may receive an instruction signal carried via conductor 44 from a host device, which is typically a computer, such as a personal computer 45, illustrated schematically FIG. 1. The printhead carriage motor and the paper handling system drive motor operate in response to the printer controller 43, which may operate in a manner well known to those skilled in the art. The printer controller may also operate in response to user inputs provided through a key pad, which may be located on the exterior of the chassis in the region generally indicated by arrow 46. A conventional monitor (not shown) coupled to the computer 45 may be used to display visual information to an operator, such as the printer status or a particular program being run on the host computer 45. Personal computers, their input devices, such as a keyboard and/or a mouse device, and monitors are all well known to those skilled in the art.

Located at one end of the travel path of carriage 38, the printer chassis 22 defines a chamber 48 that is configured to receive a service station 50 which has a frame 52. The service station 50 also has a tumbler portion 54 mounted to frame 52 for rotation when driven by a motor through an optional gear or belt assembly (not shown) that engages a drive gear 60. The tumbler 54 may support a monochrome ink cap 62 and a tri-color ink cap 64 for humidically sealing printheads 34, 36, as well as monochrome and tri-color ink wipers 66 and 68 for wiping the respective printheads 34, 36. The caps 62, 64 and the wipers 66, 68 may be of an elastomeric material, for instance a nitrile rubber, ethylene polypropylene diene monomer (EPDM) elastomer, or other types of rubber-like materials known to those skilled in the art. The wiping action may be achieved by moving the printheads 34, 36 across the wipers 66, 68. Other functions may also be provided on the tumbler 54, such as primers and the like, which are known to those skilled in the art.

The illustrated service station 50 also includes an ink collecting chamber or "spittoon" portion 70, which may comprise one or more spittoon chambers, such as a monochrome spittoon chamber 72 and a tri-color spittoon chamber 74. The spittoon chambers 72, 74 receive ink that is selectively ejected or "spit" from the respective pens 30, 32 when they are positioned above spittoon 70. It is apparent that other arrangements may be used to index the pen capping, wiping, etc. functions rather

than the tumbler 54. For example gears or linkages (not shown) known to those skilled in the art may be used for selectively engaging the service station equipment 62, 64 and 66, 68 with the respective printheads 34, 36. For instance, suitable translating or floating sled types of service station operating mechanisms are shown in U.S. Patent Nos. 4,853,717 and 5,155,497, both assigned to the present assignee, Hewlett-Packard Company.

The pens 30, 32 each include reservoirs for storing a supply of ink therein, although other ink supply storage arrangements, such as those having stationary reservoirs (not shown) mounted along the chassis may also be used. The pens 30, 32 have printheads 34, 36 respectively. Each printhead 34, 36 has a bottom surface comprising an orifice plate with a plurality of nozzles formed therethrough in a manner well known to those skilled in the art. The illustrated printheads 34, 36 are thermal inkjet printheads, although other types of printheads may be used, such as piezoelectric printheads. The printheads 34, 36 typically include a plurality of resistors which are associated with the nozzles. Upon energizing a selected resistor, a bubble of gas is formed ejecting from the nozzle a droplet of ink to form a selected image in the print zone 25.

In a conventional inkjet printing mechanism, the tri-color pen 32 contains ink in the colors of cyan, yellow and magenta, while the monochrome pen 30 contains a black ink. The types of inks that may be used in the pens 30 and 32 are pigment based inks (typically for pen 30) or dye based inks (typically for pen 32), but other types of inks may be used, such as paraffin based inks, as well as hybrid or composite inks having both dye and pigment characteristics. In the illustrated embodiment of an invisible inkjet ink printing system, one or more of these reservoirs may be filled with an invisible inkjet ink having a composition described in further detail below.

Regarding terminology used herein, the terms "invisible" and "visible" without further modifiers refer to the image being viewed under normal ambient lighting conditions, such as sunlight, conventional office lighting, or lights normally found in most homes. When an "invisible image" (invisible under ambient lighting conditions) is viewed under a beam of ultraviolet light, it becomes visible, referred to

herein with additional modifying language, such as "visible under ultraviolet light" or similar language.

For instance, FIG. 1 shows a hardcopy output as a page of paper 78 having a compound image 80 printed thereon by printer 20. The image 80 includes a visible image, such as text 82 and a border 84, and an invisible image, such as a heart 85 having a left half 86 and a right half 88. A black light 90 directs a beam of ultraviolet (uV) light 92 toward the image 80. The black light 90 has a shroud 94 which, for the purposes of this discussion, limits the travel of the ultraviolet beam 92 to the right of the image 80, as shown by the dashed lines 96. For the purposes of discussion, the remainder of the view of FIG. 1 will be considered as being lit by normal ambient light. Under these conditions, the heart's left half 86 is visible under the illumination of the black light 90, as shown in solid lines, while most of the heart's right half 88 is invisible under the normal ambient light, as shown in dashed lines. It is apparent that in the absence of visible light, the heart 85 would be more vivid and brilliant when illuminated by the black light 90 alone.

As mentioned above, one or more of the reservoirs of pens 30, 32 may be filled with an invisible inkjet ink. Indeed, different colors of invisible ink may be produced, so the tri-color pen 32 may have each reservoir filled with a different color of invisible ink, allowing printing with the pen 30 remaining filled with black ink, or the pen 30 may be filled with yet another hue or intensity of invisible ink. In these embodiment, multi-colored invisible images may be printed in conjunction with black visible images, for instance to hide an image under black text, or to print black-light posters which have some visible text, for instance, the title, author and copyright notice.

Alternatively, the monochrome pen 30 may be filled with the invisible ink, while the tri-color pen 32 is left containing the conventional cyan, yellow and magenta colored inks. In this embodiment, the color black may be printed as a composite black, where all three of the colors cyan, yellow and magenta are printed at a single location to form a black dot. This embodiment may be used to print invisible monochrome images in conjunction with multicolor visible images. It is apparent that other combinations of invisible inks with cyan, yellow, magenta and

black inks may also be used, but those described here are likely to be the most popular.

Invisible Inkjet Ink Compositions

An invisible image, such as heart 85 may be printed using an invisible inkjet ink having one or more of the formulations described below, as well as their equivalents. For instance, a variety of different invisible fluorescing dyes may be mixed with a variety of aqueous (water-based) ink vehicles to form the invisible ink, although the tested dyes and solutions are described herein. The aqueous ink vehicle is preferably selected to be compatible with commercially available cyan, yellow, magenta and black inkjet ink compositions to facilitate printing both invisible images, such as heart 85, and conventional visible images, such as text 82 or border 84, on the same sheet of media 78. Furthermore, while an aqueous ink vehicle is preferred, other types of inkjet ink vehicles may also be suitable to produce invisible inks.

The illustrated invisible inkjet ink compositions each comprise an invisible fluorescing dye plus an aqueous ink vehicle according to the following formula: (a) about 0.1 to 4 wt% (percent by weight) of at least one invisible fluorescing dye; (b) about 3 to 20 wt% of at least one diol; (c) 0 to about 5 wt% of at least one glycol ether; (d) about 3 to 9 wt% of 2-pyrrolidone; (e) about 0.5 to 5 wt% of at least one component selected from the group consisting of surfactants, buffers, and biocides; (f) about 3 to 11 wt% of at least one inorganic salt; and (g) the balance water. Excluding the dye component (a) above, the remaining components (b-g) together comprise the ink vehicle. The purity of all components is that employed in normal commercial practice for thermal inkjet inks.

A. Illustrated Aqueous Ink Vehicle Embodiment

Diols suitably employed in the practice of the invention include any of, or a mixture of two or more of, such compounds as ethanediols (*e.g.*, 1,2-ethanediol); pro-panediols (*e.g.*, 1,2-propanediol, 1,3-propanediol, 2-ethyl-2-hydroxymethyl-1,3-pro-panediol, ethylhydroxypropanediol (EHPD), *etc.*);

butanediols (*e.g.*, 1,3-butanediol, 1,4-butanediol, *etc.*); pentanediols (*e.g.*, 1,5-pentanediol); and hexanediols (*e.g.*, 1,6-hexanediol, 2,5-hexanediol, *etc.*). Preferably, 1,5-pentanediol and EHPD are employed in the practice of the invention.

The glycol ether component of the ink vehicle may comprise any of the glycol ethers and thioglycol ethers commonly employed in the inks used in inkjet printing, or a mixture thereof. Examples of such compounds include polyalkylene glycols such as polyethylene glycols (*e.g.*, diethylene glycol, triethylene glycol, tetraethylene glycol, *etc.*); polypropylene glycols (*e.g.*, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, *etc.*); polymeric glycols (*e.g.*, PEG 200, PEG 300, PEG 400, PPG 400, *etc.*); and thiodiglycol. Preferably, diethylene glycol is employed in the practice of the invention.

The preferred concentration of pentanediol and glycol component in each ink is given by the formula:

$$2x[\text{DEG}] + [\text{pentanediol}] = \text{about 6 to 10 wt\%},$$

where the square brackets denote the concentration in weight percent. For the more preferred ink vehicle compositions, DEG is absent and 1,5-pentanediol is present in the range of about 7 to 9 wt%, and most preferably about 7.5 to 8.5 wt%.

EHPD is considered separately and is present in each ink in an amount in the range of about 6 to 9 wt%. For the tested ink vehicle, EHPD is preferably present within the range of about 7 to 8 wt%.

The inorganic salt component of the present ink vehicle serves to prevent bleed between black ink and the invisible inks, and comprises one or more inorganic salts. The salts must, of course, be soluble in the ink in the concentration employed. Suitably-employed cations for the inorganic salt include alkaline earth metals of group 2A of the periodic table (*e.g.*, magnesium and calcium); the transition metals of group 3B of the periodic table (*e.g.*, lanthanum); cations from group 3A of the periodic table (*e.g.*, aluminum); and lanthanides (*e.g.*, neodymium). Preferably, calcium and magnesium are employed as cations in the practice of the invention. Suitably-employed anions associated with calcium include nitrate, chloride, acetate,

benzoate, formate, and thiocyanate, while suitable anions associated with magnesium include nitrate, chloride, acetate, benzoate, bromide, citrate, formate, iodide, sulfate, fluoride, tartrate, and thiocyanate. Inorganic salts preferably employed in the practice of the invention are the nitrate, chloride, and acetate salts of calcium and magnesium. More specifically, the cyan and magenta inks of the present invention preferably employ magnesium nitrate while the yellow ink preferably employs calcium nitrate.

The other components of the present ink vehicle, namely, surfactants, buffers, biocides, and the like, are each commonly employed additives in thermal inkjet ink compositions.

The purpose of the surfactant is to prevent color to color bleed by increasing the penetration of the inks into the print medium. Examples of surfactants that are preferably employed in the practice of the invention include secondary alcohol ethoxylates, which are nonionic surfactants, such as Tergitol 15-S-5 and Tergitol 15-S-7, which are available from Union Carbide Co. (Houston, TX). Secondary alcohol ethoxylates are nonionic surfactants and are commercially-available, for example, from Union Carbide Co. (Houston, TX) as the Tergitol series, such as Tergitol 15-S-5 and Tergitol 15-S-7.

The secondary alcohol ethoxylates contain (a) an aliphatic chain having a prescribed number of carbon atoms in the chain and (b) a prescribed number of ethoxylated units. These ethoxylates are commercially available as mixtures of ethoxylates, and so are described in terms of the predominance of a given compound. Secondary alcohol ethoxylates suitably employed in the practice of the invention predominantly have about 12 to 18 carbon atoms in the aliphatic chain, while the number of ethoxylated units is predominantly in the range of 4 to 8 units, and preferably in the range of 5 to 7 units. Thus, "Tergitol 15-S-5" represents a secondary alcohol ethoxylate surfactant predominantly having 15 carbons in its aliphatic chain and 5 ethoxylated units. A mixture of secondary alcohol ethoxylates in which the predominant number of ethoxylated units is less than 4 is not very soluble in the ink, while if the predominant number of ethoxylated units is greater than 8, the surfactant loses effectiveness in preventing color bleed.

The amount of the secondary alcohol ethoxylate preferably employed in the practice of the invention is given by the sum of the two Tergitol components, 15-S-5 and 15-S-7, according to the formula:

$$[15\text{-S-}5] + [15\text{-S-}7] = \text{about } 1 \text{ to } 4 \text{ wt\%},$$

where the square brackets denote the concentration in weight percent. Preferably, Tergitol 15-S-5 alone is present in the preferred ink vehicle in the range of about 1.5 to 3 wt% and most preferably about 1.5 to 2.5 wt%.

Optionally, a second surfactant component may be employed in the practice of the invention, namely diphenyl sulfonate derivatives, which are anionic surfactants. Rather than address the problem of bleed, the presence of this second surfactant serves to correct a sporadic problem that results in misdirected drops of ink due to puddling of ink on the nozzle plate as a consequence of different surface energies on the nozzle plate. The anionic surfactant apparently creates a substantially uniform surface energy and thus reduces the potential for misdirected drops. An example of a suitably employed diphenyl sulfonate derivative is Dowfax 8390, available from Dow Chemical (Midland, MI). Dowfax 8390 is a sodium *n*-hexadecyl diphenyl oxide disulfonate. Other sources of such diphenyl sulfonate derivatives include Pilot Chemical (Calfax 16L35), Olin Chemical (Polytergent 4C3), and Sandoz Chemical (Sandoz Sulfonate 2A1). A diphenyl sulfonate derivative may comprise up to about 0.4 wt% of the ink composition, and preferably comprises about 0.3 to 0.4 wt%.

Buffers employed in the practice of the invention to modulate pH should be organic-based biological buffers, since inorganic buffers would likely precipitate in the presence of the relatively large amount of inorganic salts in the ink composition. Further, the buffer employed should provide a pH ranging from about 6 to 9 in the practice of the invention. Examples of preferably-employed buffers include Trizma Base, which is available from, for example, Aldrich Chemical (Milwaukee, WI), and 4-mor-pholine ethane sulfonic acid (MES).

Any of the biocides commonly employed in inkjet inks may be employed in the practice of the invention, such as NUOSEPT 95, available from Hüls America

(Piscataway, NJ); PROXEL GXL, available from ICI Americas (Wilmington, Del.); and glutaraldehyde, available from Union Carbide Company (Bound Brook, NJ) under the trade designation UCARCIDE 250. PROXEL GXL is the preferred biocide.

Finally, another optional component that may be employed in the practice of the present invention is ammonium nitrate, which is used in conjunction with calcium-containing inorganic salts. Ammonium nitrate serves to prevent the precipitation of such calcium-containing inorganic salts in the ink upon exposure to the carbon dioxide in the air.

B. Illustrated Invisible Inkjet Dye Embodiments

Several different invisible inkjet ink compositions were made and tested, with the results being shown in Table 1 below for Dyes A through I, which are generally referred to herein as "invisible fluorescing dyes." It is apparent that other such invisible fluorescing dyes may also produce the desired results described herein, and thus, fall within the scope of the claims below. Images were printed on plain white paper, the most commonly available media to consumers. The resulting invisible ink compositions were then viewed under normal lighting, as well as under a black light 90, to determine their degree and color of fluorescence.

Table 1: Invisible Ink Dyes Tested
(Printed on Plain White Paper)

Dye	Dye Name	Color / Brilliance Under uV Light	Color / Brilliance for Normal Light
A	Sodium Flourescein	Yellow / Bright	Yellow / Faint
B	2,7-Dichlorofluorescein	Orange / Bright	Orange / Faint
C	Resorufin	Pink / Bright	Pink / Plain
D	Rhodamine 6G	Yellow / Bright	Yellow / Faint
E	Eosin Y, Sodium Salt	Pink / Medium	Pink / Faint

F	7-Hydroxycoumarin (Umbelliferone)	Blue / Faint	None
G	Harmine	Pink / Faint	None
H	Phloxine B	Pink / Medium	Pink / Faint
I	Salicylic Acid	Did Not Fluoresce	None

All of Dyes A through I were purchased from Aldrich Chemical Company of Milwaukee, Wisconsin. It is noted that Dyes A and B are each flourescein derivatives. All of the compounds listed above worked when blended into the illustrated ink vehicle described above, except Dye I, the salicylic acid. Dye I failed to fluoresce in the illustrated ink vehicle. It is believed that this acidic Dye I was wrongly selected, and that instead, a salt of salicylic acid, such as a sodium or potassium salt, would fluoresce when mixed with the illustrated ink vehicle, as well as with other aqueous-based ink vehicles. The manner in which these dyes were selected was based on the expected colors of fluorescence at the neutral pH of the ink vehicle. This information may be found, for instance, in Table 5-31 of Lange's Handbook of Chemistry, eleventh edition, for 58 different fluorescent dyes. The nine dyes tested were selected using Lange's Table 5-31 to obtain a range of different colors and to determine whether the fluorescent dyes were reasonably soluble in an aqueous ink vehicle. It should be noted that the resulting colors did not always match the expected colors of fluorescence listed in Lange's Table 5-31. For example, Harmine was expected to go from a blue color for an acidic pH of about 7.2, to a yellow color for a basic pH of about 8.9. Instead, the tested mixture of Harmine yielded a faint pink color under the black light 90, and it was totally invisible under ordinary ambient lighting conditions. Thus, some unexpected yet favorable results were encountered in preparing the illustrated invisible ink mixtures. It is apparent that other invisible inkjet ink dyes may also be selected using this process, and then tested as described above to determine whether they indeed do fluoresce in the selected aqueous ink vehicle.

C. Illustrated Process of

Making Invisible Inkjet Ink

In making the illustrated invisible inkjet inks, the concentration for each of the invisible fluorescing Dyes A through I was selected as 0.04% by weight of the entire ink composition. It is believed that the varying shades of brilliance listed above in Table 1 may be adjusted by varying the concentrations for the dyes to balance the brilliance of each composition with respect to others in a group. For example, dye concentrations of about 0.1 to 4 wt%, with a more preferred range being about 0.01 to 0.10 wt%, may be used to create an invisible inkjet dye set. For instance, the Dyes A, C and F may be balanced in brilliance to form an invisible ink set which may be supplied together in the tri-color pen 32 for printing "black light" posters or other artwork. It is also believed that Dyes A- H, as well as their equivalents, may be mixed to vary hue and brilliance of the resulting invisible ink composition. In some security or other applications, the various colors may be assigned different meanings.

Regarding the mixing process, all of the inks were prepared by weighing out 10 milligrams (mg) of the dye and dissolving this dye in 25 mg of the illustrated ink vehicle, having a formulation described in detail below. Stirring or shaking was done manually at room temperature for approximately five minutes to blend the dye with the ink vehicle prior to filling in an inkjet cartridge. The filled cartridge was then placed in an inkjet printer, similar to printer 20. The resulting images were printed and viewed under black light 90, with the results being shown in Table 1 above.

In these tests, the invisible inkjet ink compositions were prepared using Dyes A-H according to the following formulation and they are preferably buffered to a pH of about 7:

(a) For Dyes A through I about 0.04% wt%, which was added to a pre-mixed ink vehicle having the composition listed in items (b) through (i) below;

(b) a mixture of DEG and 1,5-pentanediol given by the formula:

$$2x[DEG] + [pentanediol] = about\ 6\ to\ 10\ wt\%,$$

and about 6 to 9 wt% ethylhydroxypropanediol (EHPD), with 1,5-pentanediol being more preferably present at about 7 to 9 wt% (and DEG absent) and most preferably about 7.5 to 8.5 wt%, and with EHPD being preferably present at about 7 to 8 wt% of the ink composition;

(c) about 3 to 9 wt% of 2-pyrrolidone, with about 6 to 9 wt% being more preferable and about 7 to 8 wt% being most preferable;

(d) about 3 to 6 wt% of a mixture of magnesium nitrate and/or calcium nitrate, with 4 to 5 wt% magnesium nitrate alone being more preferable;

(e) about 1 to 4 wt% of a mixture of Tergitol 15-S-5 and/or Tergitol 15-S-7, with Tergitol 15-S-5 being more preferably employed alone ranging from about 1.5 to 3 wt% or, most preferably, 1.5 to 2.5 wt%;

(f) up to about 0.4 wt% of Dowfax 8390 surfactant, with about 0.3 to 0.4 wt% being more preferable;

(g) about 0.1 to 1 wt% of a buffer, preferably Trizma base or MES;

(h) up to about 1 wt% of a biocide, preferably PROXEL GXL; and

(i) the balance water.

Finally, for the purposes of completeness, the black ink employed in conjunction with the present invisible ink set will be described to illustrated the compatibility of these inks when printed together on a single page 78, such as text 82 with the invisible heart 85. The black ink may be any dye-based or, more preferably, a pigment-based ink, each of which may be suitably employed in thermal inkjet printing. Suitable black dye-based inks are disclosed and claimed, for example, in U.S. Patent 4,963,189, entitled "Waterfast Ink Formulations with a Novel Series of Anionic Dyes Containing Two or More Carboxyl Groups" and assigned to the present assignee, Hewlett-Packard Company of Palo Alto, California. Suitable black pigment-based inks are disclosed and claimed, for example, in U.S. Patent 5,085,698, entitled "Aqueous Pigmented Inks for Ink Jet Printers", in U.S. Patent 5,221,334, entitled "Aqueous Pigmented Inks for Ink Jet Printers", and in U.S. Patent 5,302,197, entitled "Ink Jet Inks", all assigned to E.I. Du Pont de Nemours and Company.

We claim:

1. An invisible inkjet ink composition for printing in an inkjet printing mechanism (20), the invisible inkjet ink composition consisting essentially of an aqueous ink vehicle and about 0.01 to 4 wt% of at least one invisible fluorescing dye, which when mixed and printed through the inkjet printing mechanism (20) produce an image (85) that is substantially invisible (88) in ordinary ambient lighting conditions and viewable (86) under ultraviolet lighting conditions (92).

2. An invisible inkjet ink composition according to claim 1, wherein the invisible fluorescing dye comprises a flourescein derivative.

3. An invisible inkjet ink composition according to claim 1, wherein the invisible inkjet ink composition comprises about 0.01 to 0.10 wt% of at least one invisible fluorescing dye mixed with the aqueous ink vehicle.

4. An invisible inkjet ink composition according to any of claims 1 through 3, wherein the invisible fluorescing dye comprises at least one component selected from the group comprising:

(a) sodium flourescein;
(b) 2,7-dichlorofluorescein;
(c) resorufin;
(d) rhodamine 6G;
(e) eosin Y, sodium salt;
(f) 7-hydroxycoumarin;
(g) harmine;
(h) phloxine B; and
(i) salicylic salt.

5. An invisible inkjet ink composition according to any of the preceding claims, wherein the aqueous ink vehicle consists essentially of:

(a) about 3 to 20 wt% of at least one diol;

(b) 0 to about 5 wt% of at least one glycol ether;

(c) about 3 to 9 wt% of 2-pyrrolidone;

(d) about 0.5 to 5 wt% of at least one component selected from the group consisting of surfactants, buffers, and biocides;

(e) about 3 to 11 wt% of at least one inorganic salt; and

(f) the balance water.

6. A set of thermal inkjet inks for printing an image with an inkjet printing mechanism, with the printed image being substantially invisible in ordinary ambient lighting conditions and viewable under ultraviolet lighting conditions, the set of thermal inkjet inks comprising:

(a) a first ink;

(b) a second ink; and

(c) a third ink;

wherein each of said first, second and third inks comprises about 0.01 to 4 wt% of at least one dye selected from the group comprising (1) sodium flourescein, (2) 2,7-dichlorofluorescein, (3) resorufin, (4) rhodamine 6G, (5) eosin Y, sodium salt, (6) 7-hydroxycoumarin, (7) harmine, and (8) phloxine B; about 3 to 20 wt% of at least one diol; 0 to about 5 wt% of at least one glycol ether; about 3 to 9 wt% of 2-pyrrolidone; about 0.5 to 5 wt% of at least one component selected from the group consisting of surfactants, buffers, and biocides; about 3 to 11 wt% of at least one inorganic salt; and the balance water.

7. An invisible inkjet ink composition according to any of claims 1 through 4 or 6, wherein the aqueous ink vehicle has a formula comprising:

(a) about 6 to 10 wt% of a solvent selected from the group consisting of 1,5-pentanediol, diethylene glycol, and mixtures thereof, wherein said mixtures have the formula:

2 x (wt% diethylene glycol) + (wt% 1,5-pentanediol) = (wt% solvent);

(b) about 6 to 9 wt% ethylhydroxypropanediol (EHPD);

(c) about 3 to 9 wt% of 2-pyrrolidone;

(d) about 3 to 6 wt% of at least one inorganic salt selected from the group consisting of magnesium nitrate and calcium nitrate;

(e) about 1 to 4 wt% of at least one secondary alcohol ethoxylate surfactant predominantly having about 4 to 8 ethoxylated units and an aliphatic chain of about 12 to 18 carbon atoms;

(f) up to about 0.4 wt% of at least one diphenyl sulfonate derivative surfactant;

(g) about 0.1 to 1 wt% of a buffer;

(h) up to about 1 wt% of a biocide; and

(i) the balance water.

8. An invisible inkjet ink composition according to any of claims 1 through 4 or 6, wherein the aqueous ink vehicle has a formula comprising:

(a) about 7 to 9 wt% 1,5-pentanediol;

(b) about 7 to 8 wt% ethylhydroxypropanediol;

(c) about 6 to 9 wt% of 2-pyrrolidone;

(d) about 4 to 5 wt% magnesium nitrate;

(e) about 1.5 to 3 wt% of a secondary alcohol ethoxylate surfactant predominantly having about 5 ethoxylated units and an aliphatic chain of about 15 carbon atoms;

(f) about 0.3 to 0.4 wt% of at least one diphenyl sulfonate derivative surfactant;

(g) about 0.1 to 1 wt% of a buffer;

(h) up to about 1 wt% of a biocide; and

(i) the balance water.

9. A method for invisible printing using an inkjet printing mechanism (20) to produce a hardcopy output (78, 80) having an invisible image (85) that is substantially invisible (88) in ordinary ambient lighting conditions and viewable (86) under ultraviolet lighting conditions (92), comprising the steps of positioning a print media (78) in a printzone (25), and printing on the print media (78) in the printzone (25) with an invisible inkjet ink composition according to any of claims 1 through 8.

10. An invisible ink inkjet printing mechanism (20), comprising:

a chassis (22);

a printhead (34, 36) mounted to the chassis (22) to print in a printzone (25), the printhead (34, 36) having plural nozzles selectively fired to print a selected invisible image (85) on a print media page (78) in the printzone (25) in response to a control signal (44); and

an invisible inkjet ink composition dispensed by the printhead (36), with the invisible inkjet ink composition according to any of claims 1 through 8, to produce the selected invisible image (85) which is substantially invisible (88) in ordinary ambient lighting conditions and viewable (86) under ultraviolet lighting conditions (92).

The Patent Office

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Application No:	GB 9716006.3	**Examiner:**	Colin Sherrington
Claims searched:	1 to 10	**Date of search:**	11 November 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C4S

Int Cl (Ed.6): C09D 11/02,11/02

Other: ONLINE: WPI,CLAIMS

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	GB 1494768	(A.B.DICK COMPANY) -whole document	1 to 4, 9, 10 (at least)
X	GB 2025448 A	(UNITED STATES OF AMERICA) -whole document, especially claims 6 to 11	1, 4, 9, 10 (at least)
X	US 5286286	(XEROX CORPORATION) -whole document, especially column 8, line 50 to column 9, line 45; EXAMPLE I; claims 10 to 18	1, 9, 10 (at least)

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.